EXTENSION AND TUNING OF TOUGH2-MP EOS7R FOR THE ASSESSMENTS OF DEEP GEOLOGICAL REPOSITORIES FOR NUCLEAR WASTE: HYDROGEN, ARBITRARILY LONG DECAY CHAINS, AND SOLUBILITY LIMITS

Th. U. Kaempfer[1], Y. Mishin[1], J. Brommundt[1], J. Roger[2], E. Treille[2], N. Hubschwerlen[1]

[1]AF-Consult Switzerland Ltd, Groundwater Protection and Waste Disposal
Taefernstrasse 26, 5405 Baden, Switzerland
e-mail: thomas.kaempfer@afconsult.com

[2]Andra, Agence nationale pour la gestion des déchets radioactifs,
Parc de la Croix-Blanche, 92298 Châtenay-Malabry, France

ABSTRACT

Numerical simulation of flow and transport processes forms an important base for the assessment of the performance of deep geological radioactive waste repositories. The TOUGH2-MP simulation code with its EOS7R equation-of-state module is a good starting point for large-scale simulations of the relevant processes, including solute transport of radionuclides, in and around a geological repository.

On this base, we developed the equation-of-state module EOS75Rx that contains optimizations and specific extensions, allowing for a much more efficient treatment of the problem at hand. First, hydrogen, which is formed by corrosion of waste containers and by radiolysis of organic wastes, replaces air as the main component of the gas phase; second, an arbitrary number of arbitrarily long decay chains with branching can be considered; third, solubility limitation and associated precipitation of chemical elements are modeled; finally, a bug fix related to the source terms has been implemented.

The new TOUGH2-MP EOS75Rx module has been validated using unitary tests and benchmark problems for the single- and two-phase flow and transport of radionuclides through porous media and soils. It is currently applied to a large scale 3D simulation of the performance of a generic deep geological repository in clay host rock.

INTRODUCTION

Deep geological repositories for radioactive waste are currently being planned in several countries, including France (Andra, 2006). Among many studies to respond to the specific objectives and requirements of radioactive waste disposal, the French national agency Andra has engaged in a numerical simulation program for its deep geological repository project. The simulation program is an important tool for the conceptualization and phenomenological analysis of the future repository. It requires numerical tools that are capable of modeling appropriately the physical processes of interest in the repository and its environment. The time span of interest lasts from the constructional phase, over the operational phase with waste disposal, to the end of the post-operational phase roughly one million years later. Physical phenomena of main interest are (i) de- and re-saturation of engineered components and porous rocks, (ii) gas production due to e.g., corrosion of engineered components and subsequent migration by advection and diffusion, and (iii) release of energy and radionuclides from the waste and their transport through the engineered system, the host rock, and the embedding geological formations up to the biosphere. Furthermore, accurate models of radionuclide transport must include retardation phenomena, such as sorption or solubility limitations, and must consider radioactive decay.

From the computational point of view, the numerical tools must be highly efficient in order to allow for the simulation of very large systems as well in space as in time. For example, the

current French repository concept (Andra, 2006) consists of several thousand horizontal tunnels for the emplacement of the waste and additional tunnels and shafts for access, logistics, and ventilation during construction and operation of the repository. It encompasses a horizontal area of several kilometers in width and length, for a vertical extension of about 500 m. Moreover, the necessary phenomenological understanding and performance assessment of the repository spans over a period of up to one million years.

For the problem at hand, the parallelized program TOUGH2-MP (Pruess et al., 1999, Zhang et al., 2008) is well suited and has been used extensively in the past (e.g., Enssle et al., 2011, 2012). Within its EOS7R equation-of-state module, many of the relevant features are implemented and are ready to be used, namely the modeling of nonisothermal two-phase flow of a mixture of water, brine, air, and a two-radionuclide decay chain.

There is, however, a particular need to model arbitrarily long decay chains and consider radionuclide retardation by precipitation-dissolution, both features not available in EOS7R. Moreover, the dominant component of interest in the gas phase is often hydrogen rather than air. These requirements led us to the development of the EOS75Rx equation-of-state module.

TOUGH2-MP EOS75Rx

The TOUGH2-MP EOS75Rx module is based on the standard TOUGH2-MP EOS7R module (Pruess et al., 1999), but features (i) thermophysical properties of the water-hydrogen system instead of water-air, similar to the EOS5R module (Pruess et al., 1999), (ii) the treatment of arbitrarily long radionuclide decay chains, and (iii) retardation due to solubility limitations with precipitation-dissolution of the radionuclide components. The latter is implemented following the approach used for precipitation-dissolution of brine in the module EWASG (Battistelli et al., 1997). Moreover, the new EOS75Rx module contains a bug fix in the source-term implementation.

Hydrogen

Within a deep geological repository, the main gas of interest is often hydrogen that is formed by corrosion of waste containers and radiolysis of organic wastes. We have thus adapted the EOS7R module to consider the thermodynamic properties of the water-hydrogen system rather than that of water-air, resulting in the EOS75R module.

The adaptation required the following four properties of air being replaced by those of hydrogen: (i) molar mass, (ii) heat capacity, (iii) the viscosity model of the gas phase, and (iv) the solubility model defined by the description of Henry's constant. While the first three properties can be taken in a straightforward manner from the implementation within module EOS5, the solubility model requires some closer attention. In fact, Henry's constant is temperature dependent in EOS5 but, for the water-air system, salinity dependent in EOS7R. A detailed analysis of the new system, based on the survey study regarding solubility of gases in water and brine by Cygan (1991), showed a clear dominance of the salinity dependence in the water-hydrogen system, with the solubility model thus following the approach of EOS7R. Solubility is interpolated as a function of salinity between given values in pure water and 5N brine and independent of temperature.

Arbitrarily long decay chains

A considerable restriction of module EOS7(5)R is its mandatory consideration of exactly two radionuclides representing one parent decaying to its daughter. At least one TOUGH2 module, namely EOS9nT, can model longer decay chains (Moridis et al., 1999). However, this functionality had to be implemented from scratch within the TOUGH2-MP framework, resulting in module EOS75Rx.

The new module can treat arbitrarily long decay chains, several independent chains at the same time, and allows for branching, i.e., the decay of one parent radionuclide into several daughters.

From an implementation point of view, the extension implied the replacement of any two variables that were associated with the two radionuclides by arrays as e.g., XRN1, XRN2 by

XRN(NRN), where NRN denotes the number of radionuclides. Formulae involving explicit sums of such variables have been replaced by using implicit summation functions available in Fortran 90.

To decouple decay chains and allow for branching, two additional variables were associated to each radionuclide: an index variable specifying its parent—if existent—and a fraction of mass increase specifying the proportion of the parent decaying into the radionuclide in question (Figure 1). This approach of associating the parent to the daughter rather than the opposite was chosen to facilitate the implementation of radioactive decay.

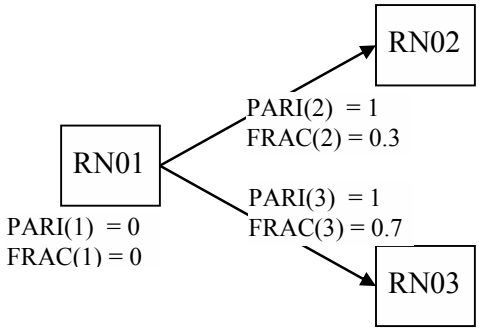

Figure 1. A parent index PARI and decay mass fraction variable FRAC per radionuclide allow for an efficient implementation of radioactive decay, including branching.

The decay chain extension also implied changes to the input functionalities of TOUGH2-MP, particularly:

- In the MULTI block, the last variable NKIN has been replaced by NRN.
- Radionuclides are numbered starting from one and labeled as RN01, RN02, … compared to their old indices 3 and 4 and labeled COM3, COM4; the hydrogen component is labeled as HYDR instead of COM5.
- The SELEC block is extended in a straightforward manner.
- Material specific distribution coefficients are defined in a new block named SORPT.

The output was intuitively adapted and includes the relevant data for all the radionuclides.

Solubility limit and precipitation-dissolution

An important retardation effect during the transport of radionuclides can be solubility limitations that result in precipitation. Given the time scales of relevance here, kinetic effects can safely be neglected and precipitation-dissolution be modeled using the so-called C_{sat} approach: Whenever, at a given location, the concentration of a radionuclide in the liquid phase would start to exceed its solubility limit C_{sat}, the radionuclide starts to precipitate and the liquid concentration remains fixed at the solubility limit. The liquid concentration is allowed to drop below the solubility limit only after all the solid phase has been dissolved again.

In some circumstances, precipitates might influence porosity and thus have a feedback on fluid flow; this is, however, neglected here. Moreover, precipitates are supposed to be immobile.

In the TOUGH2(-MP) EWASG module (Battistelli et al., 1997), solubility limitation is implemented for the brine component. This formed the basis for our implementation with respect to radionuclides in EOS75Rx. For the EWASG approach to be feasible, solubility limits are defined per radionuclide and must be independent of each other. Finally, we postulate that precipitates can exist only with a liquid phase also being present. In this case, the phase concentrations of a radionuclide are assumed to respect (i) Henry's law between the liquid and (potential) gas phase and (ii) the solubility limit between the liquid and solid phase.

With these assumptions, precipitation-dissolution can be implemented using the standard TOUGH2 approach for phase changes, namely by switching primary variables. It is implemented analogous to EWASG, as follows.

Precipitation of a radionuclide K occurs as soon as its liquid concentration C_l^K (mass per volume in the liquid phase) exceeds its user-defined solubility limit C_{sat}^K:

$$C_l^K = \frac{V_{por} S_l \rho_l X_l^K}{V_{por} S_l} = \rho_l X_l^K \; > \; C_{\mathrm{sat}}^K,$$

where $V_{por} = \phi V$ is the pore volume in an element with volume V and porosity ϕ, and

S_l, ρ_l, X_l^K are the liquid fraction, liquid density, and mass fraction of radionuclide K in the liquid phase within the element, respectively. Expressed as a condition for X_l^K, this gives

$$X_l^K > \frac{C_{\text{sat}}^K}{\rho_l}.$$

As soon as the solubility limit is reached, X_l^K is fixed and the primary variable for the radionuclide will be changed from X_l^K to the quotient between precipitated mass m_s^K and pore volume:

$$X_l^K = \frac{C_{\text{sat}}^K}{\rho_l} \ , \ X_l^K \rightarrow Z_s^K = \frac{m_s^K}{V_{por}}.$$

If variable Z_s^K decreases to zero, the precipitated phase disappears, Z_s^K is set to zero, and the primary variable switched back:

$$Z_s^K = 0 \ , \ Z_s^K \rightarrow X_l^K.$$

When phase change occurs, the new primary variable is initialized in the TOUGH2 manner using the small parameter ZERO, which is by default set to 10^{-6}. This initialization approach reduces numerical oscillation, but is not necessarily mass conservative.

As TOUGH2-MP uses the Newton-Raphson method to solve the nonlinear system of equations, checks for phase-change and associated switches of primary variables can be implemented "on the fly" using the set of secondary parameters and without changing the matrix assembling functionality of the code.

Supposing that precipitates neither modify porosity nor saturation with respect to liquid and gas phases and do not contribute to internal energy, the mass- and energy-balance equations solved by TOUGH2-MP (Pruess et al., 1999) require only minor adaptations to account for the additional solid phase. For example, the mass accumulation term for radionuclide K, which is implemented as a sum over phase contributions

$$M^K = \phi \sum_\beta S_\beta \rho_\beta X_\beta^K,$$

with $\beta \in \{l, g, s\}$ the phase index and S, ρ, X the saturation degree, density, and mass fraction, respectively, can be written as

$$M^K = \phi\left(S_g \rho_g X_g^K + S_l \rho_l X_l^K + Z_s^K\right).$$

Precipitation-dissolution capability necessitated extending the TOUGH2-MP input functionalities, particularly as follows:

- Solubility limits are input using a new block called SOLUL that is repeated for each material that has solubility limitation for at least one radionuclide.
- For initial conditions and the SAVE format, the potential presence of precipitates is specified using flags. For each element, after the usual set of initial conditions for the primary variables, a line with a list of logical flags ('T' for True and 'F' for False) of length NRN is added (e.g., 'TFFTF' for five radionuclides with the first and fourth one present in solid form).

The output was intuitively adapted and includes all the relevant data of the potential three phases per radionuclide.

Mass conserving source terms

In standard TOUGH2(-MP), transient source terms are not necessarily interpreted in a mass and energy conserving way, depending on the choice of the interpolation scheme with MOP(12). This has been corrected for in EOS75Rx with new options MOP(12) = 3,4,5 corresponding to mass conservative implementations of the interpolation schemes MOP(12) = 0,1,2.

CODE VALIDATION

Hydrogen

The EOS75R module with the water-hydrogen system has been validated by comparison with module EOS5 for single-phase liquid, single-phase gas, and two-phase conditions. For appropriate choices of temperature that short-circuit dependencies in EOS5, the results must be and are identical up to rounding errors between the two modules. To test salinity dependence of solubilities in two-phase conditions, we have successfully compared simulated fractions of dissolved hydrogen for brines with different molarities to the fractions expected from the conceptual model.

Solubility limit and long decay chains

The new EOS75Rx module has, for all functionalities already available in EOS75R, been thoroughly tested, using an extensive non-regression test series available at AF-Consult Switzerland Ltd. The new features of precipitation-dissolution and arbitrarily long decay chains were evaluated first using several unitary tests and second on a more complicated physico-numerical test case (see next section).

A simple unitary test, consisting of four Finite Volumes, external no-flow boundary conditions for all components, and a radionuclide source that is first positive, then negative at constant rates in all elements, demonstrates the precipitation-dissolution feature (Figure 2). The liquid concentration increases from the start at a constant rate. As soon as the solubility limit is reached, the liquid concentration remains fixed and the solid concentration increases at the same rate as the liquid concentration did before. The inverse behavior occurs in the second half of the test, when the source is negative. Total mass balances have been successfully compared between a case with and one without solubility limit.

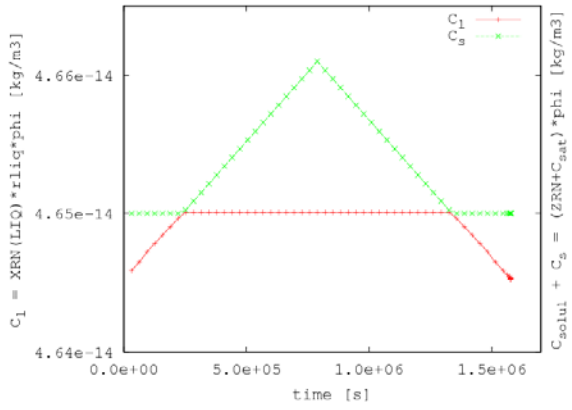

Figure 2. Evolution of radionuclide concentration (liquid in red left, solid in green right) in the very simple four-element test case. The concentrations have been calculated from 'liquid mass fraction XRN(LIQ)', 'liquid density rliq', 'solid mass per pore volume ZRN', and 'porosity phi' and the solid concentration was shifted by the solubility limit.

As a more complex test case, we designed a vertical "one-dimensional" column of saturated Callovo-Oxfordian clay with dimension 1×1×50 m that was discretized by 250 Finite Volumes. Fixed pressures of 5×10^6 Pa and 6×10^6 Pa at the top and bottom of the column, respectively, induced a pressure gradient and slight upward flow. The column was either fully saturated or had an initial saturation of 0.9 and was allowed to resaturate from the top. We considered the simple decay chain $^{245}Cm\rightarrow{}^{241}Pu$ and defined a source with a release rate of 10^{-13} kg·s^{-1} for the parent radionuclide in the bottom-most Finite Volume and over the whole simulation period of 2 000 years. However, in order to test a precipitation-dissolution process that is decoupled from the release rate, and in order to trigger precipitation after a relatively short simulation time, we modified the radionuclide properties such that ^{245}Cm had no solubility limit and a short half-life, while ^{241}Pu did decay only very slowly. This led to a situation where the solubility limit of the daughter radionuclide was reached after around 500 years.

We compared qualitatively the concentrations (Figures 3 and 4) and quantitatively the mass balances of the two radionuclides between a simulation without and one with solubility limit of the daughter radionuclide.

a) no solubility limit b) with solubility limit

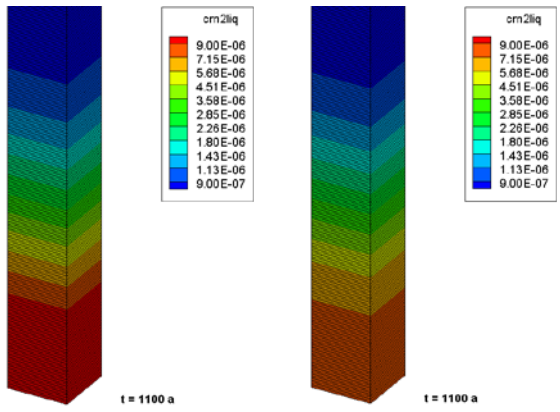

Figure 3. Liquid concentration (in kg per m^3 overall volume) of the daughter radionuclide for the fully saturated situation without (left) and with (right) solubility limit.

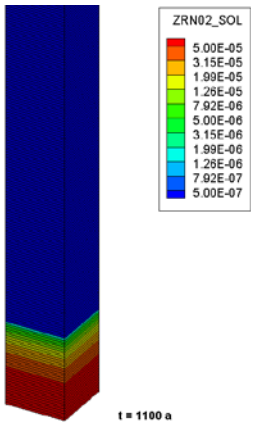

Figure 4. Solid concentration (in kg per m^3 pore volume) of the precipitating daughter radionuclide for the fully saturated case.

PHYSICO-NUMERICAL TEST-CASE

We considered the two-dimensional transport of radionuclides from a schematic representation of half of an emplacement cell for radioactive waste embedded in Callovo-Oxfordian clay (Figure 5). At time zero, the emplacement cell is partially desaturated and it resaturates over time from the host rock inwards. We considered the 4N+1 radionuclide decay chain

$$^{245}Cm \rightarrow ^{241}Pu \rightarrow ^{241}Am \rightarrow ^{237}Np \rightarrow ^{233}U \rightarrow ^{229}Th,$$

where ^{245}Cm is released at a constant rate for the first 100 years.

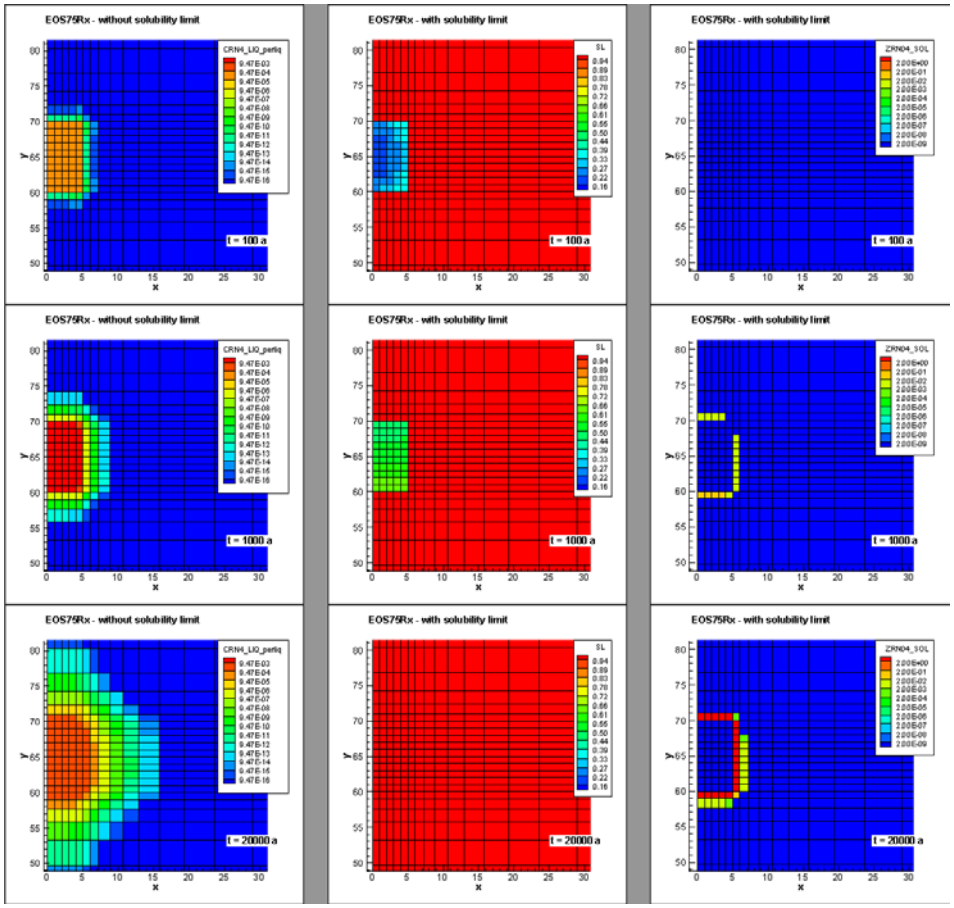

Figure 5. Evolution of the liquid concentration of ^{237}Np (in kg per m^3 liquid volume, left), the liquid saturation (middle), and the solid concentration of ^{237}Np (in kg per m^3 pore volume, right) for the physico-numerical test-case with solubility limitations in an area close to the emplacement cell.

We performed two simulations up to 20,000 years, one without solubility limitation and one for which the radionuclide solubility limits were set to their reference values in Callovo-Oxfordian clay. In particular, for ^{237}Np a solubility limit of 4×10^{-6} mol·l^{-1} was imposed.

For the case with solubility limitation, the evolution of the liquid concentration of ^{237}Np, the saturation level, and the mass of precipitates is shown in Figure 5. As can be seen, the solubility limit of ^{237}Np is reached in the host rock in Finite Volumes close to the emplacement cell.

In the present test-case, only the solubility limit of ^{237}Np is reached. The radionuclide concentrations are thus identical between the two simulations for the first three radionuclides in the decay chain. The retardation effect due to precipitation is best seen for ^{237}Np (Figures 6 and 7), but prevails also for the further decay products ^{233}U and ^{229}Th.

In summary, the present physico-numerical test case demonstrates the capability of TOUGH2-MP EOS75Rx for treating long decay chains with retardation by precipitation.

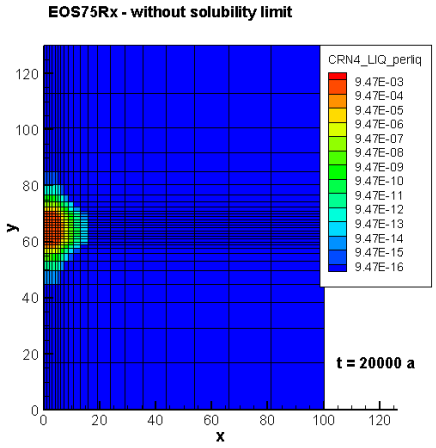

Figure 6. Distribution of the liquid concentration of ^{237}Np (in kg per m^3 liquid volume) at the final simulation time for the physico-numerical test-case without solubility limit. Shown for the full computational domain.

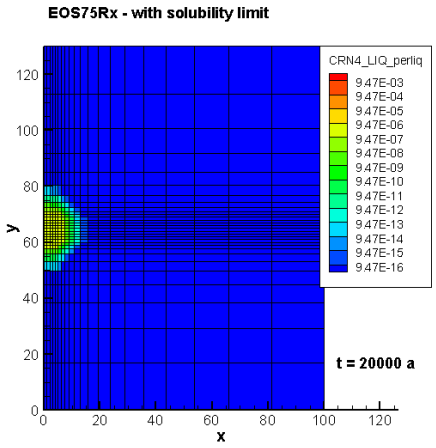

Figure 7. Distribution of the liquid concentration of ^{237}Np (in kg per m^3 liquid volume) at the final simulation time for the physico-numerical test-case with solubility limit. Shown for the full computational domain.

PERFORMANCE

The implementation within the EOS75Rx module, when compared to the EOS7(5)R module, uses array variables associated with the radionuclides instead of two individual variables for radionuclide one and two. Moreover, many computational formulae have been rewritten using intrinsic summation functions of Fortran 90.

Solving the physico-numerical test-case described above for a decay chain of two radionuclides, we consistently observe an improvement in performance from module EOS7(5)R to EOS75Rx of approximately 10%. Similar performance increases are seen for more advanced benchmark problems. In the case of computations with only one radionuclide, performance is further increased, since in this case the EOS75Rx module indeed considers just one radionuclide, while the original TOUGH2-MP EOS7R module always builds up a system that includes two radionuclides.

CONCLUSION

We built a new TOUGH2-MP equation-of-state module, called EOS75Rx, based on the EOS7R module, but which considers hydrogen as the primary gas phase instead of air. This allows for arbitrarily long radionuclide decay chains to be considered, has retardation by precipitation-

dissolution implemented, and contains a bug fix within the source term implementation. The module has been thoroughly tested using an extensive set of nonregression and unitary tests, and its capabilities have further been demonstrated using a two-dimensional physico-numerical test case. A performance increase of approximately 10% has been observed in our new module compared to module EOS7(5)R.

The module is currently applied to large-scale simulations of radionuclide release for the French deep geological repository concept.

ACKNOWLEDGMENT

The developments of the EOS75Rx module and part of this publication have been funded by Andra. Valuable input was provided by Carl-Philipp Enssle. Thanks to Keni Zhang who kindly responded to questions regarding TOUGH2-MP.

REFERENCES

Andra, *Dossier 2005 Argile – Synthesis – Evaluation of the feasibility of a geological repository in an argillaceous formation,* ISBN: 2-916162-00-3, 2006.

Battistelli, A., C. Calore, and K. Pruess, *The simulator TOUGH2/EWASG for modelling geothermal reservoirs with brines and non-condensible gas,* Geothermics, Vol. 26, No. 4, pp. 437-464, 1997.

Cygan, R. T., *The solubility of gases in NaCl brine and a critical evaluation of available data,* Report SAND90-2848, Sandia National Laboratories, Albuquerque, New Mexico, 1991.

Enssle, C.P., J. Croisé, A. Poller, G. Mayer, and J. Wendling, *Full scale 3D-modelling of the coupled gas migration and heat dissipation in a planned repository for radioactive waste in the Callovo-Oxfordian clay*, Physics and Chemistry of the Earth, DOI: 10.1016/j.pce.2011.07.033, 2011.

Enssle, C.P., J. Brommundt, Th. U. Kaempfer, G. Mayer, and J. Wendling, *Full scale 3D modelling of a repository in the Callovo-Oxfordian clay with focus on two-phase transport of ^{14}C and ^{129}I,* submitted to Proceedings of 'Clays in Natural & Engineered Barriers for Radioactive Waste Confinement', October 2012, Montpellier, France, 2012.

Moridis, G. J., Y.-S. Wu, and K. Pruess, *EOS9nT: A TOUGH2 module for the simulation of water flow and solute/colloid transport in the subsurface,* Report LBNL-42351, Lawrence Berkeley National Laboratory, Berkeley, California, 1999.

Pruess, K., C. Oldenburg, and G. Moridis, *TOUGH2 user's guide, version 2.0*, Report LBNL-43134, Lawrence Berkeley National Laboratory, Berkeley, California, 1999.

Zhang, K., Y.-S. Wu, and K. Pruess, *User's Guide for TOUGH2-MP – A massively parallel version of the TOUGH2 code*, Report LBNL-315E, Lawrence Berkeley National Laboratory, Berkeley, California, 2008.